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Preparation of high-purity lead oxide from spent lead paste by low temperature burnt and

hydrometallurgical with ammonium acetate solution

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Abstract: Lead sulfate, lead dioxide and lead oxide are the main component of lead paste in the spent lead-acid battery. And, there are a few part of impurities in spent lead paste which have great influence on the performance of the new battery, so it is necessary to removed. In this paper, a novel approach with low temperature burnt and hydrometallurgical by NH_4AC is developed to recovered lead from spent lead paste. Firstly, a part of impurities were converted to metal oxide by the calcinations of spent lead paste at low temperature. Secondly, the metal oxides are transformed into soluble sulphate which is produced by the reaction between calcination products and dilute H_2SO_4 and H_2O_2 (5.0%). Then, separate the solid from solution by filtration, the solid is mainly $PbSO_4$ $BaSO_4$ and $CaSO_4$, and NH_4AC is used as the leaching solution of $PbSO_4$ and introduces CO_2 to obtain purity $PbCO_3$. Under the optimized leaching conditions (leaching temperature at 40°C for 20 min, 10.0wt.% NH_4AC), the lead recovery ratio is about 99.9%. The calcination product of lead carbonate is PbO, and high-purity lead oxide had been achieved. The initial discharge capacity of high-purity lead oxide is about 158 mAh g^{-1}, and the capacity loss is less than 2% after 80 cycles.

1. Introduction

The production of lead is growing fast in China, but the growth rate of secondary lead production is slow. The annual lead production in China increased from 1.2 million tonnes (MT) in 2001 to 4.64 million tonnes (MT) in 2013 [1]. In 2013, the lead production was about 3.28 MT and the secondary lead production was only about 1.36 MT in China. And, the percentage of secondary lead in total lead production was 29.7% which is less than the industrial developed country. This is because the technology of China's secondary lead was backward and the scales of the plants were generally small. Meanwhile, the recovery of China's secondary lead is low efficiency and high pollution.

As we know, the consumption of lead acid batteries accounts for 84% of lead consumption [2], and its lifecycle is generally two years [3]. This results generated large amounts of scrap lead-acid batteries and the number is constantly increasing every year. The scrap amount accounts for more than 90% of scrap lead in the whole society [4]. Hence, from the perspective of environmental protection, no matter what level the lead industry developed, it should take more attention to recycle of the scrap lead acid battery. It is necessary to design a recovery process with environment friendly and low energy consumption [5].

A typical spent lead acid battery mainly consists of four components: waste electrolyte, polymeric materials, lead alloy grids and lead paste [6]. Among these, lead paste is the most difficult part to deal with. The mainly element of spent lead paste are lead sulfate (~60%), lead dioxide (~28%), lead oxide (~9%), metallic lead (~3%) and a small amount of impurities such as iron, antimony, tin and barium [7]. Environmentally sensitive recovery of spent lead paste has attracted considerable interest from researchers [8-10].

Recently, more increasing attention has been paid to the recovery of spent lead paste on alternative

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hydrometallurgical process. Generally, spent lead paste is desulfurized by using salt solution [11-14] or organic

acid [8-9]. PbO_2 is the second most high constituent in the spent lead paste and be reduced to Pb (□) to aid

subsequent leaching by using H_2O_2 (aq), $FeSO_4$ or $Na_2S_2O_3$. Nedialko K. Lyakov et al [15] firstly proposed the

investigation of the desulphurization process of spent lead paste by sodium carbonate and sodium hydroxide, the

results show that the desulphurization process of spent lead paste goes at a higher speed when using NaOH to

replace Na_2CO_3. X. Zhu et al. [16] worked out a sustainable method, with minimal pollution and low energy cost

in comparison with the conventional melting methods, is proposed for treating components of spent lead-acid

battery pastes in aqueous organic acid. In his studies, spent lead paste was treated with an aqueous acetic acid

(CH_3COOH) and sodium citrate $(Na_3C_6H_5O_7 \cdot H_2O)$ solution to generate lead citrate precursor which was then

separated from the solution. However, in these previous researches, the impurities in spent lead pastes can easily

join and contaminate the precursor, sometimes leading to unacceptably high content impurities in the final leady

oxide. And then, the capacity retention ratio of the batteries manufactured with the leady oxide as the active

material of the cathode decreases rapidly after 20~30 cycles. The impurities in the leady oxides powder could lead

to the deterioration of the battery cycle performance [17-19]. It is urgent to develop a new green lead recovery

process with lower energy consumption and obtain high-purity lead oxide without or with low content of

impurities. Herein, Junqing Pan et al. [13] reported a new green hydrometallurgical process for producing

high-purity metallic Pb based on a specially designed H_2-PbO fuel cell. The PbO was recovered from the spent

lead paste by a desulfurization of lead sulphate and a redox reaction of Pb and PbO_2 with a catalyst. But, the

processes of H_2-PbO fuel cell have not yet been adopted by the industry.

The aim of this paper is to prepare high purity lead oxide for lead-acid battery by a new production process.

Lead sulfate, lead dioxide and lead oxide are the main components of lead paste in the spent lead-acid battery. And,

there is a small part of impurities in spent lead paste, which is needed to be removed. In this paper, a novel

approach by low temperature burnt and hydrometallurgical with ammonium acetate was developed to recovery high-purity lead oxide from spent lead paste. Furthermore, the impurities in spent lead paste could be removed by calcinaing-dissolving-separating procedure, the researchers did not more consider this issue in previous reports.

2. Experimental

2.1. Experimental Materials

The sample of spent lead pastes were provided by a secondary lead smelting plant in Hunan Zhuzhou, China. Before calcinations, the spent lead paste was washed by distilled water to remove electrolyte. The chemical compositions of the spent lead paste is shown in Table 1. The spent lead paste in this paper are exclusive of metal lead (Pb), because metal lead (Pb) will be oxidized to lead oxide (PbO) after washing, drying and milling.

Fig.1 presents the XRD of the spent lead paste before calcinations, which shows the components of spent lead paste are $PbSO_4$, PbO_2, PbO and others (Sb, FeS, $CaSO_4$ and $BaSO_4$). Concentrtated sulfuric acid (H_2SO_4, 98%) was used to prepare the dilute H_2SO_4 solution with distilled water. Hydrogen peroxide (H_2O_2, 5.0%) was used as the reductive agent. Ammonium acetate (NH_4AC) was used as the desulfate agent during leaching of precipitate after filtration.

2.2. Experiment Methods

The objective of this work was to seek a new method to obtain high-purity lead oxide from spent lead paste. Flow sheet of this process is schematically shown in Fig.2. After calcinations, the solids were reacted with H_2SO_4 and H_2O_2. Then, through filtrating to removed impurities elements of Fe and Sb, the solid will continued to react with NH_4AC solution and almost dissolved. After filtration, $Pb(AC)_2$ solution was obtained and without other impurities elements of Ba and Ca. The solution reacted with CO_2 to get $PbCO_3$. And finally, decompose it at low

temperature to obtained high-purity PbO powder.

A schematic diagram of the electric resistance furnace is shown in Fig.3. The spent lead paste powder was put in a porcelain crucible, which was placed in the electric resistance furnace. In order to make the impurities in spent paste be completely oxidation, we introduce oxygen enriched air during calcination process. The temperature in furnace was elevated to a given calcinations temperature (300 ~ 400°C) by 5°C·min⁻¹, and the spent lead paste was calcined in a given time at the designated calcinations temperature in the furnace. Finally, refrigerate the calcined sample to room temperature.

After calcination, the samples reacted with dilute H_2SO_4 (1.08g mL⁻¹) at 40°C for 2h, followed stirring. Metal oxides would reacted with sulfuric acid (H_2SO_4) completely, and produced soluble sulfate. Meanwhile, adding 5.0% hydrogen peroxide (H_2O_2) as the reductant for PbO_2. The compounds of lead will exist as the form of lead sulfate. After filtration, the solid that comprised barium sulfate ($BaSO_4$), calcium sulfate ($CaSO_4$) and lead sulfate ($PbSO_4$) was obtained. An aqueous solution of ammonium acetate (NH_4AC) was used as the desulphurizing agent to react with $PbSO_4$ in solid. The reaction (1) is based on the fact that $PbSO_4$ with CH_3COO^- can form complex ion $(CH_3COO)_3 Pb^-$ in NH_4AC solution.

$$PbSO_4(s) + 2CH_3COONH_4(aq)= (CH_3COO)_2Pb(aq) +(NH_4)_2SO_4(aq) \tag{1}$$

In the desulphurizing experiment, the effects of the NH_4AC concentration, reacting temperature and reacting time on the recovery rate, were investigated. And then, after filtration, the filtrate can be used directly for produced $PbCO_3$ by introducing CO_2. The precipitate and filtrate through filtration can get lead carbonate crystals. The recovery rate of lead from spent lead paste was calculated through the follow Eq. (2), (3), (4) and (5).

$$(CH_3COO)_2Pb(aq) + CO_2 + H_2O = PbCO_3(s) + 2CH_3COOH(aq) \tag{2}$$

$$\text{Recovery Rate of Lead} = \frac{m_{1(Pb)}}{m_{2(Pb)}} \times 100\% \tag{3}$$

$$m_{1(Pb)} = m_1 [w_1 \frac{M_{r(Pb)}}{M_{r(PbSO_4)}} + w_2 \frac{M_{r(Pb)}}{M_{r(PbO_2)}} + w_3 \frac{M_{r(Pb)}}{M_{r(PbO)}}] \tag{4}$$

$$m_{2(Pb)} = m_2 \frac{M_{r(Pb)}}{M_{r(PbCO_3)}} \tag{5}$$

Where m_1 is the mass of original spent lead paste, w_1 is the mass percentage of $PbSO_4$, w_2 is the mass percentage of PbO_2, w_3 is the mass percentage of PbO, m_2 is the mass of $PbCO_3$.

Finally, the high-purity lead oxide was prepared by the calcination of lead carbonate in air at 405˚C for 2h, that is based on the thermodynamics analysis.

2.3. Characterization of materials

The phase composition of the different leady oxides was determined by X-ray diffraction (XRD) analysis using D/MAX 2550 X-ray diffraction analyzer (Japan) with Cu Kα radiation (λ=1.54 nm) at 80 mA and 5.0 kV. The crystal morphology of the different leady oxides was examined by scanning electron microscopy (SEM) technique using an environmental scanning electron microscope ESEM Quanta-200FEG FEI (Holland)

2.4. Battery assembling and testing procedure

The methods of battery assembling and testing are based on our previous work reported in the literature [20]. In battery assembling (Fig.4), the lead oxide powder products act as positive active material, while negative plates were provided by commercial sources. After mixing, pasting, curing and formation processes, each of the dried positive plates was coupled with two commercial negative plates soaked in sulfuric acid solution (1.28 g cm^{-3}) electrolyte so that batteries for testing under 2 V/0.2 Ah could be made. Both the charging and discharging cycle tests were performed repeatedly at a constant current of 25 mAh with a cut-off terminal voltage of 1.75 V (depth of discharge, DOD = 100%).

3. Result and discussion

Fig.5 shows the detailed process flow chart of preparing high-purity lead oxide from spent lead paste. The

main ideas of this paper was to calcined spent lead paste in low temperature, dissolve calcination products in

H_2SO_4 and H_2O_2, and then desulphurize it by NH_4AC to get $PbCO_3$ crystal, finally high-purity PbO was

prepared from $PbCO_3$ by low temperature burnt.

3.1. Pretreatment of spent lead paste

When spent lead paste was calcinated in electric resistance furnace (Fig.3) with oxygen-enriched air, a part of

impurities would react with O_2 to produce metallic oxide ($M + O_2 \rightarrow M_2O_x$). According to the experimental

analysis, the components of calcination products were different in different time and temperature. For example,

the impurities were incompletely oxidized in 300°C for 2 h, and the impurities were completely oxidized in 400°C.

Taking energy into consideration, high calcination temperature will cause energy waste. Therefore, after carrying

multi-groups calcination experiments, the optimum burning condition was identified as 405°C for 2h. The XRD

pattern, photographic and SEM image of the calcinations product are shown in Fig.6 and Fig.7 (b). Compared

with the XRD pattern of spent lead paste (Fig.1), after low temperature burnt, Sb and FeS were changed to Sb_2O_3

and Fe_2O_3. The calcination reactions of spent lead paste under oxygen-enriched air are listed as follows:

$4Sb + 3O_2 = 2Sb_2O_3$ (6)

$4FeS + 7O_2 = 2\ Fe_2O_3 + 4SO_2$ (7)

And, the color of calcination product changed obviously, compared with original spent lead paste. After

calcining, the particle size of calcination product had an evidently agglomerated.

Fig.7 (c), (d) and Fig.8 present the SEM images and XRD pattern of the solid which was calcinations reacted

with H_2SO_4 and H_2O_2. The components of the solid were $PbSO_4$ and minute quantity $BaSO_4$ and $CaSO_4$.

Compared with calcination product, the impurities in the sample powder were decreased. Because Sb_2O_3 and

Fe_2O_3 were reacted with H_2SO_4 to produce soluble sulfate. And, lead oxide generated lead sulfate in H_2SO_4 solution. The main reaction principles were as follow:

$$Sb_2O_3 + 3H_2SO_4 = Sb_2(SO_4)_3 + 3H_2O \tag{8}$$

$$Fe_2O_3 + 3H_2SO_4 = Fe_2(SO_4)_3 + 3H_2O \tag{9}$$

$$PbO + H_2SO_4 = PbSO_4 + H_2O \tag{10}$$

$$PbO_2 + H_2O_2 + H_2SO_4 = PbSO_4 + 2H_2O + O_2 \tag{11}$$

After filtration, the soluble sulfate [$Sb_2(SO_4)_3$, $Fe_2(SO_4)_3$] was existed in filtrate. $PbSO_4$ was the main component in precipitate. The SEM images of precipitate are shown in Fig.7 (c), (d), it can be seen that the precipitate has an irregular structure with an average size. The particle size was about 100 nm, much smaller than that of the original spent lead paste. Therefore, the precipitate has a higher specific surface area which is good for desulphurization reactions in next experiment.

3.2. Hydrometallical desulfurization of $PbSO_4$

According to the chemical reaction mechanism diagram, lead sulfate was dissolved in ammonium acetate (NH_4AC) solution, and generated soluble lead acetate [$Pb(AC)_2$]. Introducing carbon dioxide (CO_2) into $Pb(AC)_2$ solution will produce white precipitate ($PbCO_3$). As we know, the decomposition temperature of lead carbonate is lower than lead sulfate, and the lead carbonate ($PbCO_3$) can readily convert into lead oxide (PbO) by thermal decomposition at a relatively low temperature about 400 ˚C. Meanwhile, this method can avoid the emission of harmful sulfur oxides (SO_2).

Fig.9 (a) presents the effect of reaction temperature on the variation of the recovery rate of lead from $PbSO_4$. As shown in Fig.9, complete precipitation is not achieved, and the recovery rate of lead from $PbSO_4$ increase from 88.69% at 20 ˚C to 98.55% at 40 ˚C. It indicates that the reaction temperature has a significant effect on the

recovery efficiency. When the reaction temperature increases (50 ˚C), the recovery rate of lead does not change. A reaction temperature of 40 ˚C is found to be optimal for hydrometallical desulfurization of $PbSO_4$.

When the reaction temperature was 40 ˚C, the effect of reaction time on the lead recovery rate of $PbSO_4$ was presented in Fig.9 (b). Generally, lead recovery rate increased with the increase of the reaction time. When the reaction time is long enough, almost all the $PbSO_4$ can be converted. And, the recovery efficiency of lead could reach up to 98.0% at 20min. After 20min, the recovery efficiency of lead was almost invariable. Thus, it is reasonable to settle 20 min as the optimal reaction time.

The effect of concentration of NH_4AC solution on recovery rate of lead is shown in Fig.9. As shown in Fig.9, the recovery rate increased when the concentration of NH_4AC solution increased. The recovery efficiency can reach up to nearly 99.0% at 10% NH_4AC solution and then efficiency is constant with any further thicker NH_4AC solution. In summary, the optimal desulfurization conditions of $PbSO_4$ are: a reaction temperature of 40 ˚C, reaction time of 25 min and 10 wt.% NH_4AC solution. Under the optimal conditions (reaction time of 20min, reaction temperature of 40 ˚C and concentration of NH_4AC of 10 wt.%) the lead recovery rate can reach up to 99.0%. The solid residue in the solution after desulphurize process consists of a small amount of un-converted $PbSO_4$ and other insoluble solid impurities ($BaSO_4$ and $CaSO_4$).

3.3. Characterization of the precursors

The lead acetate solution has been obtained by desulfuration of $PbSO_4$ as previous discussed. There are many ways to recovered lead from the lead salt solution. Karami et al. [21] discussed the synthesis of nano-structured lead oxide through reacting with lead nitrate solution and sodium carbonate solution by the sonochemical method. In this paper, recovering lead from lead acetate solution was carried out by a precipitation reaction where the slurry was produced by introducing carbon dioxide in solution. The carbonation can be summarized as Eq. (12).

$$Pb(AC)_2 + CO_2 + H_2O = PbCO_3 (\downarrow) + 2HAC \qquad (12)$$

After filtering, the precipitate product was dried at 100 ˚C for 8h. The XRD pattern of the precipitate product is shown in Fig.10 (a), which is a pure lead carbonate pattern according to the standard card (JCPD File NO. 70-2052) [22]. The SEM image of the precipitate product of lead carbonate is shown in Fig.11. As shown in Fig.11, the distribution of particle size is in the range of 0.5 μm - 1.5μm.

The TG curve of $[Pb(AC)_2]$ is shown in Fig.10 (b). There is only one weight loss step in the temperature range 321 ˚C~400 ˚C. The weight loss at 321 ˚C~400 ˚C can be described as the decomposition of the lead carbonate. The weight loss is about 17.0%, which is close to the theoretical value (16.47%, base on Eq. (13)). This weight loss was due to the decomposition of lead carbonate to generate lead oxide because the oxidation number of the lead ions is constant during the thermal decomposition process.

$$PbCO_3 \triangleq PbO + CO_2(\uparrow) \qquad (13)$$

The XRD patterns of the calcined products from lead carbonate are shown in Fig. 10 (a). The results showed that the lead carbonate was decomposed completely at the temperatures of 405 °C for 2 h. As shown in Fig. 10 (a), the lead carbonate has been converted to a crystalline phase of PbO (JCPDS File No.87- 0604) [23-24]. No significant impurities were observed, which indicates that pure lead oxide was obtained. The SEM image of the calcined product (PbO) from lead carbonate is shown in Fig.11. As shown in Fig.11, the morphology of the calcined products exhibited crystals in the size of 100 nm, much smaller than that of the barton-pot leady oxide. The smaller particle can provide a large contact area of active material for the electrochemical reactions to proceed, which is beneficial for battery performance.

The spent lead paste can be used to produce lead oxides powders after simple chemical conversion steps. The purity of lead oxide product prepared in low temperature calcinations is about 99.5%. This simple recycling method for waste lead acid battery paste has a positive effect on the recovery of lead oxide from the starting

materials of spent lead paste. Meanwhile, compared with other methods, the particle size of high-purity PbO is

much smaller. D. Yang et al. [18] have reported that the calcinations products from lead citrate precursor particles

are 400 nm. Mayer [25] has investigated the influence of the particle size on battery performance. Their results

indicate that the oversize leady oxide do great harm to the battery cycle performance. In our previous researches

pure lead oxides could be directly used as the positive active materials for new lead-acid batteries [20,26].

3.4. Battery performance

In this experiment, batteries were assembled by different leady oxide powder (factory leady oxide and

high-purity lead oxide). Fig.12 gives the first discharge curves of cell voltage versus capacity at a current density

of 30 mA g^{-1}. It is evident that, the initial discharge capacity of the high-purity lead oxide is about 158 mAh g^{-1},

while factory leady oxide is about 143 mAh g^{-1}. Therefore, the high-purity lead oxide has a higher discharge

capacity than factory leady oxide because of its larger specific surface area. As we know, the theoretical capacity

of pure PbO is 240 mAh g^{-1}, and the utilization of active material is defined as the ration of the discharge capacity

and the corresponding theoretical capacity of PbO. The utilization of high-purity PbO is about 65.8%, which is a

higher discharge capacity in lead acid battery [27].

Cycle performance of batteries manufactured by factory leady oxide and high-purity lead oxide are shown in

Fig. 13. The capacity retention ratios of the assembling batteries made from the two kinds of lead oxide products

show a good cyclic stability in 80 charge/discharge cycles with the depth of discharge of 100%. It can be seen that

the discharge capacity of high-purity PbO was quite stable in the 80 cycles. In general, good cycling performance

mostly depends on the excellent of the active material particles and their large specific surface area, which will

enhance their reactivity with sulphuric acid readily. It can be seen that the high-purity PbO comprises much

smaller paricles and has a closely packed structure, this type of scattered granular crystal structure facilitates the

expansion of the plate and reduces the stability of the plate structure. The cycle performance of the assembled batteries in this study is significantly better than previous reported that using the novel lead oxide recovered from the spent lead pastes with the acetic and sodium citrate leaching process [18].

Therefore, removing impurities in the recovery lead oxide has more important influences on the performance of the new battery. In summary, high-purity PbO is a superior material for the manufacture of high-quality lead acid batteries with a longer cycle life and a higher discharge capacity. The experimental results are of significance in order to develop economic and environmental processes for the recycle of spent lead acid battery.

4. Conclusion

In this work, a new, environmentally friendly route to replace the traditional spent lead paste smelter recycling operation is proposed. Furthermore, this method improves the hydrometallurgy technique as previous reported. It is an urgent requirement to develop a new green lead recovery process with lower energy consumption without the use of toxic chemicals, and achieve high-purity lead oxide.

(1) Spent lead paste burnt in low temperature can make some impurities (Sb, Fe) converted into metal oxide, and reacted with H_2SO_4 to generate soluble salt. Meanwhile, the main components of spent lead paste all turned to lead sulfate.

(2) Desulfurization of lead sulfate by NH_4AC solution and the thermal decomposition of lead carbonate precursor have been carried out in laboratory scale. The effects of time, temperature and concentration of NH_4AC on the recovery efficiency were investigated. Under optimal conditions (reaction time of 20 min, reaction temperature of 40 ˚C and concentration of NH_4AC of 10 wt.%), the lead recovery rate can reach up to 99.0%. After that, other impurities (Ca, Ba) are removed and pure $PbCO_3$ and high- purity PbO are obtained.

(3) Battery testing results reveal that initial discharge capacity and cycle life of lead acid battery

manufactured by high-purity lead oxide are better than that of factory leady oxide. The initial discharge capacity

of high-purity lead oxide is about 158 mAh g^{-1}, and it behaves excellently in terms of cyclic stability. The capacity

loss is less than 2% in 80 cycles when it is full discharged at 30 mA g^{-1}.

(4) In further work, we will investigate the recovery impurities from spent lead paste. Improve resource

recovery rate and utilization.

Acknowledge

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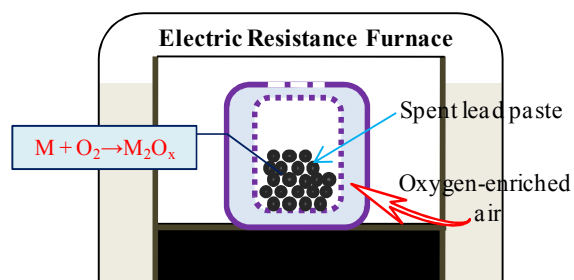[27] P. Gao, Y. Liu, X. Bu, M. Hu, Y. Dai, X. Gao, L. Lei. J. Power Sources 242（2013） 299-304.

Fig.1. XRD pattern and image of the spent lead paste before calcination.
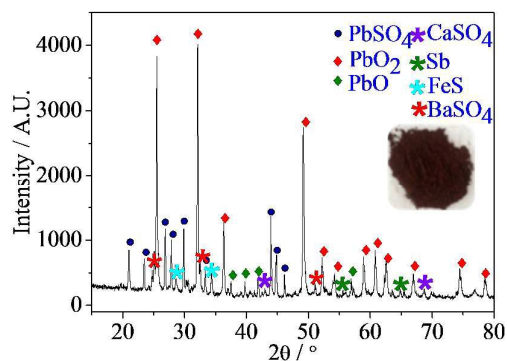
Fig.2. Process flowsheet of preparation of high-purity PbO from spent lead paste.
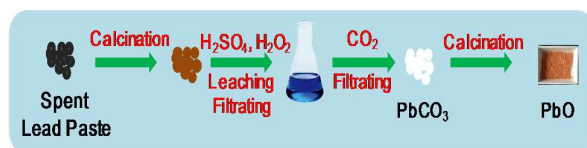
Fig.3. Schematic diagram of the electric resistance furnace.

Fig.4. Assumption diagram of the assembly of lead acid battery in laboratory.

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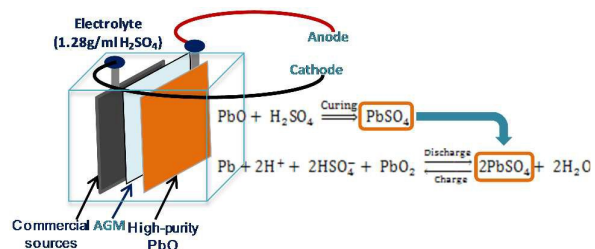
Fig.5. Detailed process flow chart of prepared high-purity lead oxide from spent lead pas
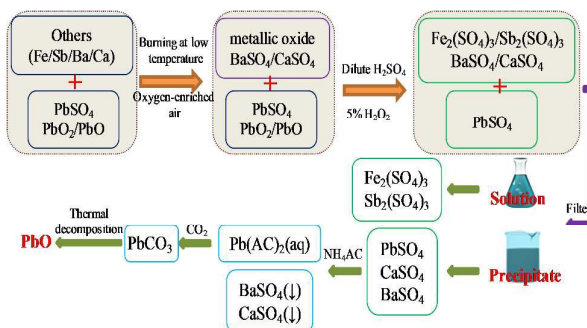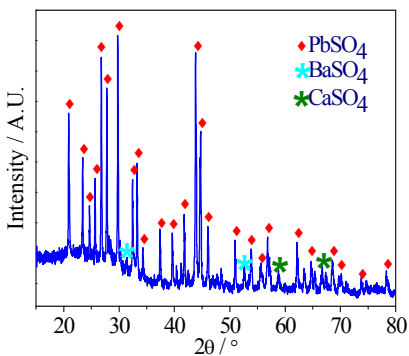

Fig.6. XRD pattern and photographic of the calcinations product of spent lead paste.
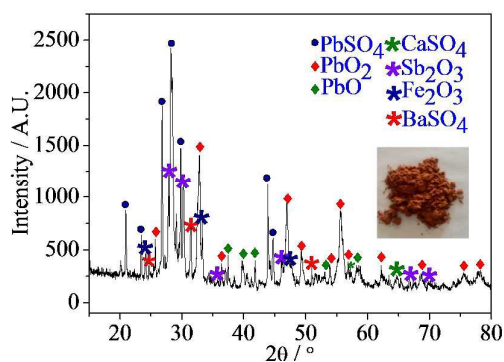
Fig.7. SEM image of spent lead paste (a) and calcinations product (b) and precipitate(c), (d) that was the product

of calcinations react with H_2SO_4 and H_2O_2.

2
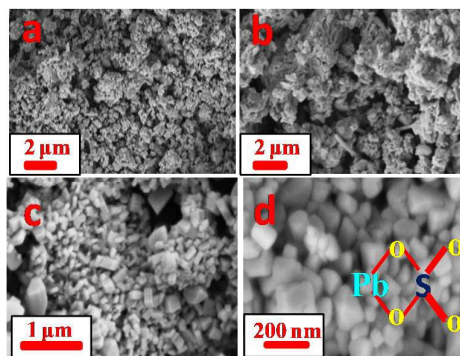
**Fig.8.** XRD pattern of precipitate that was the product of calcinations product with H_2SO_4 and H_2O_2.


Fig.9. The chemical reaction mechanism diagram of this process; effect of time, temperature and concentration of ammonium acetate on the lead recovery rate of desulphurization.
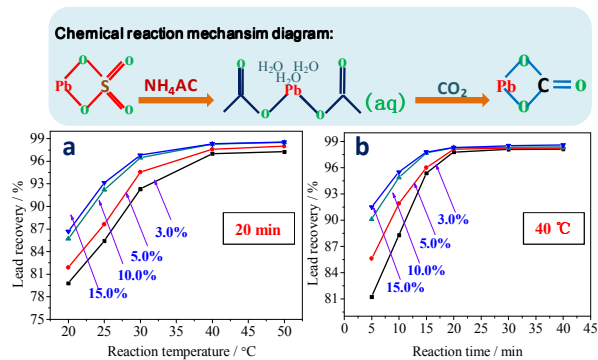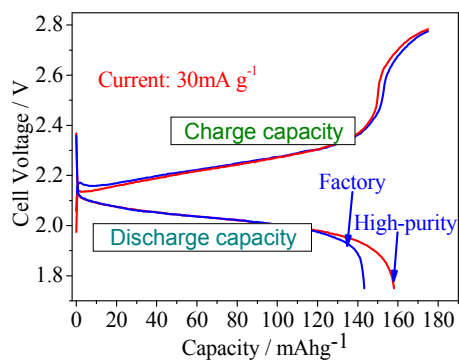

Fig.10. (a) XRD patterns and photographs of the lead carbonate and lead oxide; (b) TG curve of the lead carbonate decomposition in air;
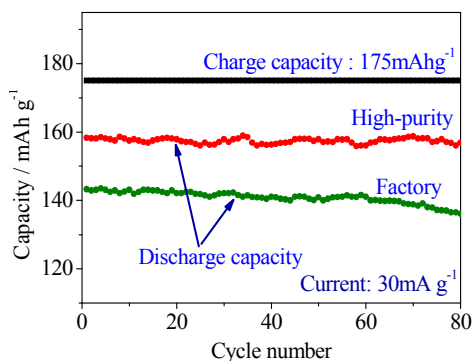

3
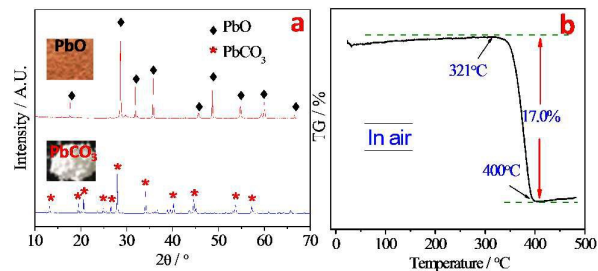
Fig.11. SEM images of the lead carbonate product (PbCO$_3$) and calcined product (PbO).
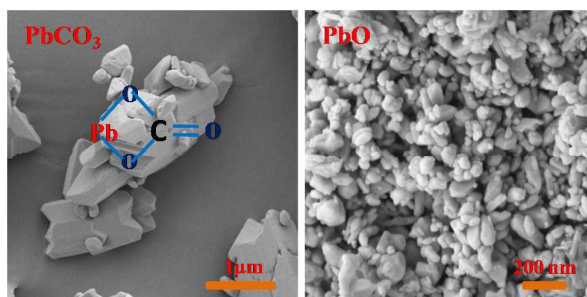
Fig.12. Initial discharge capacity of batteries assembled with factory leady oxide and high-purity lead oxide.

Fig.13. Cycle life of batteries assembled with factory leady oxide and high-purity lead oxide.

Table 1 Chemical composition of spent lead paste.

	Spent lead paste				
Element	Pb	Sb	Fe	Ba	Ca
%	70.75	0.037	1.120	2.89	0.656